BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 333—334 (1973)

The Reductive Coupling Reactions of Some Chloromethylbenzene Derivatives with Iron(II) Complexes. II. Reduction by Anhydrous Iron(II) Chloride and Lithium Chloroferrate(II)

Kazuhiko ONUMA, Junzo YAMASHITA,* and Harukichi HASHIMOTO*
Department of Synthetic Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo
**Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Sendai*

(Received March 7, 1972)

Previously we reported[1] that ferrous chloride tetrahydrate reduces polyhalomethylbenzene derivatives to give coupling products.[2] Though some chelating ligands such as ethylenediamine can increase the yield of coupling products considerably,[1] hydrolysis by the water of crystallization or solvolysis by the ethanol solvent of the organic halides is unavoidable in these reactions, and this limits, in some cases, the synthetic usefulness of this reaction.[1,2]

To inhibit the side reactions, therefore, we prepared anhydrous ferrous chloride and lithium chloroferrate(II)—$LiFe^{II}Cl_3$—in acetonitrile as will be described in the Experimental Section[3] and investigated the reaction with organic halides.

TABLE 1. REDUCTIVE COUPLING OF BENZOTRICHLORIDE BY FERROUS CHLORIDE AND LITHIUM CHLOROFERRATE(II) IN ACETONITRILE

$FeCl_2$: 1.0×10^{-2} mol, $LiFeCl_3$: 2.0×10^{-2} mol, CH_3CN: 60 ml

Fe(II)	$PhCCl_3$: Fe	Temp. °C	Time hr	Product[a] (%)	
				$PhCCl_2$-CCl_2Ph	PhCCl=CClPh
$FeCl_2$	1:1	80	5	51	—
	1:2	80	5	77	—
$LiFeCl_3$	1:1	50	5	74	—
	1:2	80	4	—	87[b]

a) Yield based on $PhCCl_3$ used.
b) Isomer ratio is *trans*: *cis*=33: 67.

TABLE 2. REDUCTIVE COUPLING OF DIPHENYLDICHLOROMETHANE BY FERROUS SALTS

$FeCl_2$: 1.0×10^{-2} mol, $LiFeCl_3$: 2.0×10^{-2} mol, CH_3CN: 60 ml

Fe(II)	Ph_2CCl_2: Fe	temp. °C	time hr	Product[a] (%)	
				Ph_2CCl-$CClPh_2$	Ph_2C=CPh_2
$FeCl_2$	1:1	20	22	51[b]	—
	1:2	80	5	—	64[b]
$LiFeCl_3$	1:2	80	4	—	93

a) Yield based on Ph_2CCl_2 used.
b) Benzophenone and unreacted diphenyldichloromethane were recovered. The former is the product by hydrolysis of the latter during the after-treatment of the reaction mixture.

TABLE 3. REDUCTIVE COUPLING OF BENZAL CHLORIDE BY FERROUS SALTS

$FeCl_2$: 1.0×10^{-2} mol, $LiFeCl_3$: 2.0×10^{2-} mol, CH_3CN: 60 ml

Fe(II)	$PhCHCl_2$: Fe	Temp. °C	Time hr	product[a] (%)	
				PhCHCl-CHClPh	*trans*-PhCH=CHPh
$FeCl_2$	1:1	80	4	3[b]	6[c]
	1:2	80	24	—	28[c]
$LiFeCl_3$	1:1	30	24	5[b]	6[c]
	1:2	80	7	—	81

a) Yield based on $PhCHCl_2$ used.
b) *meso*-Isomer.
c) Benzaldehyde and unreacted benzal chloride were recovered. See the footnote b) in Table 2.

The results are tabulated in Tables 1—3. We wish to point out that reductive coupling products are obtainable in good yields without any competing side reactions. The use of the anhydrous salt is evidently superior to the use of the tetrahydrate; in the latter case, some additives are needed for good results.[1] In addition, anhydrous lithium chloroferrate(II) has been revealed to be the more powerful reductant. Thus, tolan tetrachloride is obtained from benzotrichloride by $FeCl_2$, but if $LiFeCl_3$ is employed (Fe(II)/$PhCCl_3 \geq 2$), benzotrichloride is further reduced to tolan dichloride, with a shorter reaction time than the $FeCl_2 \cdot 4H_2O$–DMSO system.[2]

Tetraphenylethylene is generally attained from diphenyldichloromethane by the use of ferrous salt under ordinary conditions (Table 2), and tetraphenyldichloroethane has been thought to be formed only intermediately. Reaction at a low temperature with $FeCl_2$, however, gave tetraphenyldichloroethane in a considerable yield.[4] Thus, it is seen that the highly selective reductive coupling of benzotrichloride and of diphenyldichloromethane is possible by the use of $FeCl_2$ or $LiFeCl_3$ in acetonitrile.

As may be seen in Table 3, the attempt to obtain stilbene dichloride from benzal chloride in a good yield failed (only 3% by $FeCl_2$ and 5% by $LiFeCl_3$). However, *trans*-stilbene was obtained in a high yield by employing $LiFeCl_3$ as the reductant. It should be

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[1] K. Onuma, J. Yamashita, and H. Hashimoto, This Bulletin, **43**, 836 (1970).

[2] Similar results were reported in T. Shirafuji, Y. Yamamoto, and H. Nozaki, *ibid.*, **44**, 1994 (1971).

[3] M. Asscher and D. Vofsi, *J. Chem. Soc., B*, **1968**, 947.

[4] This attempt failed in previous studies because of the hydrolysis of the organic halide by the water of crystallization in $FeCl_2 \cdot 4H_2O$. The $FeCl_2 \cdot 4H_2O$–DMSO system gave also tetraphenyldichloroethane in a good yield at a low temperature with a smaller $FeCl_2 \cdot 4H_2O/Ph_2CCl_2$ mole ratio.[2]

noted that the $FeCl_2 \cdot 4H_2O$–CH_3CN[1] or –DMSO system[2] failed to obtain *trans*-stilbene from benzal chloride. All these reductions are thought to proceed step by step as follows;

$$\mathrm{Ph(R)CCl_2} \xrightarrow{\mathrm{2Fe(II)}} \mathrm{Ph(R)CCl\text{-}CCl(R)Ph}$$

$$\xrightarrow{\mathrm{2Fe(II)}} \mathrm{Ph(R)C{=}C(R)Ph}$$

$$(\mathrm{R=Ph,\ Cl,\ H})$$

The reduction of benzyl chloride by $LiFeCl_3$ was also attempted, but only 4% of bibenzyl resulted. Benzyl bromide was converted to benzyl chloride under the same conditions.

As may be seen, the reactivity of lithium chloroferrate(II) is obviously superior to that of ferrous chloride. This may be partly due to the fact that $FeCl_4^-$ ion is very stable in acetonitrile.[5]

Experimental

Materials. The anhydrous ferric chloride and iron powder were used directly. The benzotrichloride, benzal chloride, benzyl chloride, and diphenyldichloromethane were distilled under reduced pressure and then used. The purification of acetonitrile was done in the following manner: it was distilled first from potassium permanganate and sodium carbonate, second from phosphorous pentoxide, and at last carefully under nitrogen from calcium hydride after reflux. The lithium chloride was dehydrated *in vacuo* at 150°C for several days.

Preparation of the Ferrous Solution. To a solution of anhydrous ferric chloride (2.6 g) and, if necessary, lithium chloride (1.02 g) in acetonitrile (70 ml), iron powder (1.8 g) was added under an atmosphere of nitrogen according to the Asscher and Vofsi method.[3] After standing for several hours, the solution was filtered and introduced into the reaction vessel. The concentration of the solution was determined by ceric titration just before the reaction. The concentration of chloride ions in the lithium chloroferrate solution was determined by Volhard's method. The $FeCl_2$ solution is almost colorless or slightly yellow, and the $LiFeCl_3$ solution is faintly violet. As these iron salts are very sensitive to air, they should be treated carefully in a nitrogen atmosphere.

Reaction Procedure. In a four-necked, 100 ml flask equipped with a nitrogen inlet, a thermometer, a magnetic stirrer, and a condenser, a 60 ml portion of a ferrous solution was introduced ($FeCl_2 = 1 \times 10^{-2}$: $LiFeCl_3 = 2 \times 10^{-2}$ mol/l): the reaction was then initiated by adding organic halide at the required temperature under nitrogen. After the completion to the reaction, 150 ml of water was poured in and then extracted with benzene. The benzene solution was then condensed, and the coupling products were isolated. The resinous by-products were removed through column chromatography (300 mesh alumina). All the products were recrystallized and identified by mp, IR NMR, and elemental analysis.[1]

Mixture of *cis*- and *trans*-tolan dichloride were separated by means of the difference in their solubility to alcohol, and the separated isomers were again recrystallized from alcohol. The melting point of the *trans* isomer is 145.0—146.0°C, while that of the *cis* isomer is 59.0—62.0°C. The melting point of tetraphenyldichloroethane is 161—167°C.

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[5] B. J. Hathaway and D. G. Holah, *J. Chem. Soc.*, **1964**, 2408.